



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

A Rapid Compression Machine Modelling Study of the Heptane Isomers

E. J. Silke, H. J. Curran, J. M. Simmie, W. J. Pitz,
C. K. Westbrook

May 23, 2005

European Combustion Meeting
Louvain-la-Neuve, Belgium
April 3, 2005 through April 6, 2005

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

A Rapid Compression Machine Modelling Study of the Heptane Isomers

Emma J. Silke¹, Henry J. Curran and John. M. Simmie

*Department of Chemistry
National University of Ireland, Galway
Ireland.*

William J. Pitz and Charles K. Westbrook

Lawrence Livermore National Laboratory, Livermore, California 94551, USA.

Abstract

Previously we have reported on the combustion behaviour of all nine isomers of heptane in a rapid compression machine (RCM) with stoichiometric fuel and ‘air’ mixtures at a compressed gas pressure of 15 atm. The dependence of autoignition delay times on molecular structure was illustrated. Here, we report some additional experimental work that was performed in order to address unusual results regarding significant differences in the ignition delay times recorded at the same fuel and oxygen composition, but with different fractions of nitrogen and argon diluent gases.

Moreover, we have begun to simulate these experiments with detailed chemical kinetic mechanisms. These mechanisms are based on previous studies of other alkane molecules, in particular, n-heptane and iso-octane. We have focussed our attention on n-heptane in order to systematically redevelop the chemistry and thermochemistry for this C₇ isomer with the intention of extending our greater knowledge gained to the other eight isomers. The addition of new reaction types, that were not included previously, has had a significant impact on the simulations, particularly at low temperatures.

Introduction

The key to being able to improve the efficiency, performance and emissions of combustion systems is a better understanding of the chemistry involved over a wide range of temperatures and pressures. Therefore there is much interest in understanding the oxidation of hydrocarbons; such as the heptane isomers, under a broad range of conditions, and more specifically the low temperature chemistry involved in the oxidation of these fuels [1–7]. n-Heptane has long been used as a model fuel for two reasons. The first is that in SI engines it is a component of the primary reference fuels, which are used to determine octane numbers. Secondly, it has been used for experiments and modeling studies of diesel engines as it has a cetane number that is typical for diesel fuel, and therefore its combustion and ignition properties are similar to those of diesel.

We have recently reported rapid compression machine (RCM) experimental data for all nine heptane isomers under stoichiometric conditions, at a compressed gas pressure of 15 atm and in the temperature range 600–960 K [8]. This was the first complete investigation of the nine isomers in the same study, although other studies have presented data for a number of the C₇ isomers in a small number of experimental set-ups [5,7]. Reliable data of this nature are essential for understanding how fuel structure affects autoignition and combustion processes in kinetically controlled modes such as Homogeneous Charge Compression Ignition (HCCI). Such data are also important to validate and refine chemical kinetic models of these processes.

Previous modelling work by Westbrook *et al.* for the heptane isomers includes calculation of ignition delay

times behind reflected shock waves for each of the nine isomers in the temperature range 1190–1428 K [9], but there was no experimental data available against which the model predictions could be validated. In a related study, Westbrook *et al.* prepared detailed chemical kinetic mechanisms for all nine isomers under rapid compression [10]. Therefore our purpose is to extend this study to the preparation of accurate simulations using comprehensive chemical kinetic models [11] for the combustion of the complete set of heptane isomers using the recorded ignition data [8] and other data in the literature for validation.

Experimental Update

Previously we have reported on the combustion behaviour of all nine isomers of heptane with stoichiometric fuel and ‘air’ mixtures at a compressed gas pressure of 15 atm in a rapid compression machine with creviced piston heads [8]. Since then, it has been concluded that the creviced piston heads in use for these measurements are near optimal as regards to temperature field homogeneity [12].

In order to investigate, in detail the autoignition behaviour of the heptane isomers, the compressed gas temperature range of 600–960 K was studied [8]. This was done by varying the proportions of the diluent gases (N₂, Ar) so as to alter the overall heat capacity ratio of the fuel and diluent ‘air’ mixture resulting in the range of compressed gas temperatures studied. In addition, a thermostat fitted to the combustion chamber allowed the initial temperature to be varied independently. For each of the nine isomers of heptane, three fuel and ‘air’ mixtures were investigated to cover this compressed gas temperature range; the lowest temperatures using pure

¹ Email: emma.silke@nuigalway.ie

nitrogen as diluent (600–725 K), intermediate temperatures using a 50:50 mixtures of nitrogen and argon (700–825 K) and the highest temperatures using argon only (800–950 K). This means that there was an overlap of some of the compressed gas temperatures investigated, with the only variation being the actual mixture diluent composition at these particular temperatures.

The adiabatic compressed gas temperature, T_C , and pressure, p_C , were calculated based on ideal theory from the initial temperature, initial pressure and the volume ratio of the RCM (0.0952) [8]. Results were presented in terms of the overall dependence of ignition delay time (ms) on the compressed gas temperature (K), for each fuel and ‘air’ mixture studied for all nine isomers of heptane, and we believe that the diluent gas effect we observed has not been reported previously. It was reported that ignition delay times were recorded at the same T_C for different diluents and that ignition delay times at these T_C values were longer with higher argon diluent concentration. Figs. 1 and 2 illustrate this point quite clearly. Ignition delay times recorded at a T_C of 820 K for the 0.50 N_2 / 0.50 Ar mixtures are shorter than for the mixture with pure argon as diluent for both 2,3- and 3,3-dimethylpentane (DMP).

Following publication of the results of our original investigation [8], two major updates have been applied:

1. The compressed gas temperature (T_C) was calculated based upon the recorded p_C reached within the combustion chamber, rather than using the initial temperature, initial pressure and compression ratio in order to account for non-ideality of the system.
2. In an effort to resolve the question of variation in ignition delay times at the same T_C for different diluent compositions, some new fuel and ‘air’ mixtures were prepared — intermediate in composition to those previously investigated. The results of these are presented and discussed here.

For 2,3-DMP a fuel in ‘air’ mixture of 0.25 N_2 / 0.75 Ar was examined, Fig 1. At compressed gas temperatures of 680–700 K ignition delay times lie between those for pure nitrogen and 0.50 N_2 / 0.50 Ar diluent.

In addition, a 3,3-DMP fuel in ‘air’ mixture of 0.25 N_2 / 0.75 Ar was examined, Fig 2. At compressed gas temperatures of 750–850 K ignition delay times lie between those for 0.50 N_2 / 0.50 Ar diluent and those for pure argon as diluent.

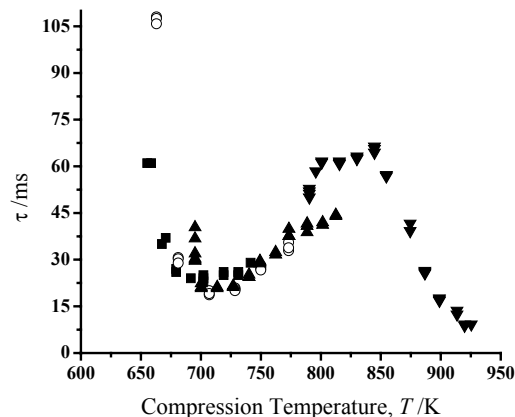


Fig. 1 1.87% 2,3-dimethylpentane (RON = 91.1), $\phi = 1.0$, p_C approximately 15 atm, ■ N_2 only, ○ N_2 / Ar 0.75 / 0.25 [new data], ▲ 0.50 N_2 / 0.50 Ar, ▼ Ar only.

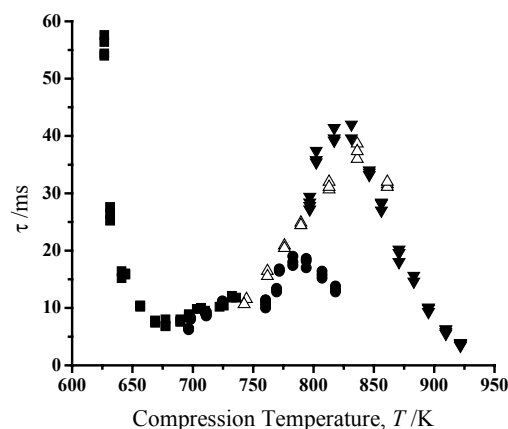


Fig. 2 1.87% 3,3-dimethylpentane (RON = 80.8), $\phi = 1.0$, $p_C \approx 15$ atm, ■ N_2 only, ● 0.50 N_2 / 0.50 Ar, Δ 0.25 N_2 / 0.75 Ar [new data], ▼ Ar only.

These additional experimental results clearly show that the previous data was not anomalous and that ignition delay times *do* get longer with increasing Ar fraction. The source of this behaviour may be due to the heat capacities, and/or the thermal diffusivities of nitrogen and argon. However, the thermal diffusivities of both nitrogen and argon are very similar and so this behaviour depends mainly on the difference in heat capacities. A mixture with nitrogen as diluent will maintain a higher temperature for longer than an otherwise identical mixture with argon diluent. Hence, the ignition delay time for the argon mixture will be ‘stretched out’ and will result in a longer ignition delay time at the same compressed gas temperature. Tables 1 and 2 show ignition delay times measured at the same temperature for different diluent compositions. As the argon composition increases the ignition delay time also increases.

Fuel / 'Air' Mixture	Temperature (K)	Time (ms)
23DMP/ O ₂ / N ₂ : Ar 3/4 : 1/4	773	33.8
23DMP/ O ₂ / N ₂ : Ar 1/2 : 1/2	773	38.4

Table 1. Comparison of ignition delay times for 2, 3-DMP at almost identical T_C , with the variation in diluent composition.

Fuel / 'Air' Mixture	Temperature (K)	Time (ms)
33DMP/ O ₂ / N ₂ : Ar 1/2 : 1/2	794	18.2
33DMP/ O ₂ / N ₂ : Ar 3/4 : 1/4	790	24.4
33DMP/ O ₂ / Ar	796	27.8

Table 2. Comparison of ignition delay times for 3, 3-DMP at almost identical T_C , with the variation in diluent composition.

Essentially, we conclude that there is no *one* smooth curve of ignition delay time versus temperature for a fuel over the entire temperature range under investigation. Ignition delay times are a function of the heat losses occurring due to the mixture composition.

Modelling

Kinetic modelling for n-heptane was performed using the HCT (Hydrodynamics, Chemistry and Transport) program [13], which solves the coupled chemical kinetic and energy equations, and permits the use of a variety of boundary and initial conditions for reactive systems depending on the physical nature of the system being examined. The THERM program of Ritter and Bozzelli [14], employing group additivity methods developed by Benson [15], was used to determine thermochemical quantities for all the chemical species for which there were no available data.

Initially, work has been directed towards the systematic redevelopment of the low temperature mechanism, which has been published previously for n-heptane and iso-octane [16,17], beginning with new reaction types. The additions of these reaction types, or classes as we refer to them here, were not included in these previous studies. Such reaction classes investigated included the following:

1. O₂QOOH = alternative H-atom isomerization
2. O₂QOOH → cyclic Ether + OH
3. RO₂ + OH → RO + HO₂
4. RO₂ + HO₂ → ROOH + O₂
5. RO₂ = QOOH (New rate constants)
6. O₂QOOH = Ketohydroperoxide + OH (New rate constants)
7. QOOH intra-molecular isomerizations

As we will show, not all the reaction classes investigated proved to be sensitive within the scope of our study.

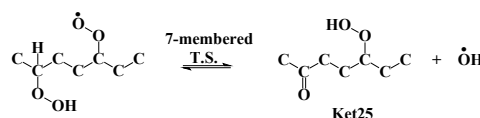
Original Mechanism:

Curran *et al.* originally published a mechanism for n-heptane oxidation in 1998 [16] in which they described rate constant rules for the various reaction classes

associated with fuel oxidation, particularly under low temperature conditions. This work was updated in 2002 with a study of iso-octane oxidation [17], with many of the thermochemical properties and rate constant expressions adjusted.

In their previous studies of n-heptane and iso-octane Curran *et al.* [16,17] considered only one internal H-atom isomerization step for O₂QOOH to produce a stable carbonyl- or keto-hydroperoxide species and a hydroxyl radical. This reaction involves the migration of the H-atom from the carbon atom attached to the hydroperoxyl group to the peroxy radical site, an example of which is shown in Fig. 3 (a).

(a) Reaction Type 23 [14]



(b) Alternatives (this work)

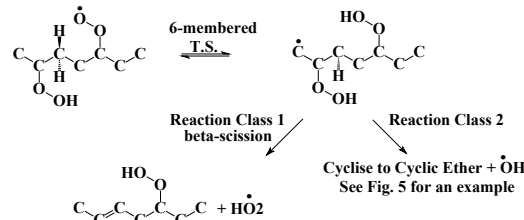


Fig. 3 Detailed chemistry for O₂QOOH: (a) example of the type of isomerization considered by Curran *et al.* [16,17] and (b) additional isomerizations considered in this work.

It was argued by Curran *et al.* that this hydrogen atom, Fig. 3 (a), is weaker than a typical hydrogen atom in a hydrocarbon species and is more easily abstracted. However, ring-strain energies dictate that in many instances other conventional hydrogen atoms, which may form a 6-membered transition state ring for example, are also available. Rate constant analysis has shown that these alternative reactions are indeed competitive, or even faster, than the formation of the ketohydroperoxide and a hydroxyl radical.

Reaction Class 1: O₂QOOH ⇌ Alternative H-atom isomerization

In order to include this chemistry the species associated with reaction class 1 were generated from O₂QOOH isomerizations, Fig. 3 (b), along with the related reactions and then added to the original mechanism. These alternative reactions lead to the formation of an alkene-hydroperoxide species and a hydroperoxyl radical rather than a ketohydroperoxide species and a hydroxyl radical. This leads to a significant change in the mechanism prediction. Fig. 4 shows predictions of the previous mechanism [17] together with the updated mechanism with these “alternative” O₂QOOH H-atom

isomerizations added. Previous predictions gave reasonably good agreement with experimental data. However, it is clear that the addition of these alternative reactions leads to longer ignition delay times than previously predicted in the temperature range 600–850 K, and an overall decrease in the performance of the kinetic mechanism. However, we can account for this decrease in reactivity by the increased concentration of less reactive HO₂ radicals in comparison to more reactive hydroxyl radicals. The new chemistry added had little or no effect on the mechanism predictions at temperatures above 850 K, as the H₂O₂ (+M) = OH + OH (+M) branching reaction predominates in this intermediate temperature range [18].

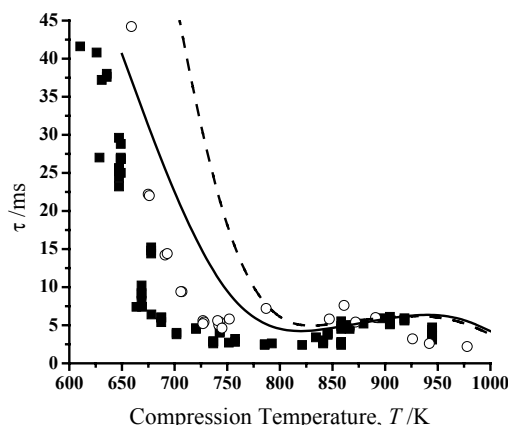


Fig. 4 The 2002 Curran *et al.* mechanism (solid line) [17], versus updated mechanism with reaction class 1 - alternative O₂QOOH internal H-atom isomerizations (dashed line), Galway RCM data ■ [8] and Griffiths *et al.* RCM data ○ [5] for 1.87% n-heptane, $p_c = 10$ atm, $\phi = 1.0$.

Reaction Class 2: O₂QOOH → Cyclic Ether + OH

This reaction class had not previously been included in the mechanism of Curran *et al.* [16,17]. For n-heptane, we permit the formation of five-, six-, seven- and eight-membered transition state rings.

This has led to the addition of 90 new species and 177 new reactions. Fig. 5 shows the formation of these species from an arbitrary O₂QOOH species.

This reaction class leads to the formation of a stable alkyl-peroxide cyclic-ether species and a hydroxyl radical. This new reaction scheme competes with the “alternative” isomerization reaction (reaction class 1, which produces hydroperoxyl radicals) and so leads to an increase in reactivity at lower temperatures, Fig. 6, which results in better agreement with the experimental results at 15 atm [8].

However, the predicted ignition delay times are still substantially longer than those measured experimentally in the temperature range 625–800 K.

Example of 6-membered transition

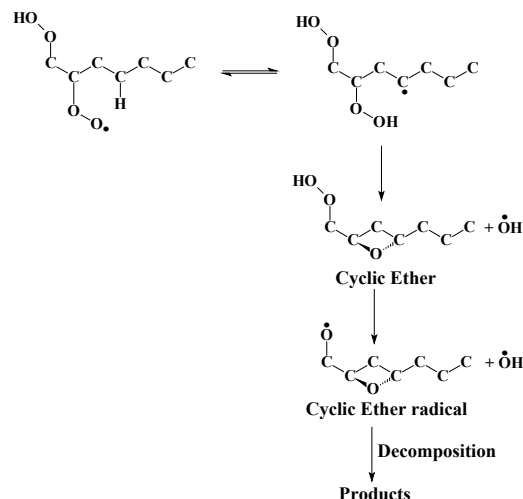


Fig. 5 Reaction scheme for Reaction Class 2: the formation of Cyclic Ether + OH from O₂QOOH species. In this example a 6-membered ring transition of 1C₇H₁₄OOH—2O₂ is used to illustrate the chemistry.

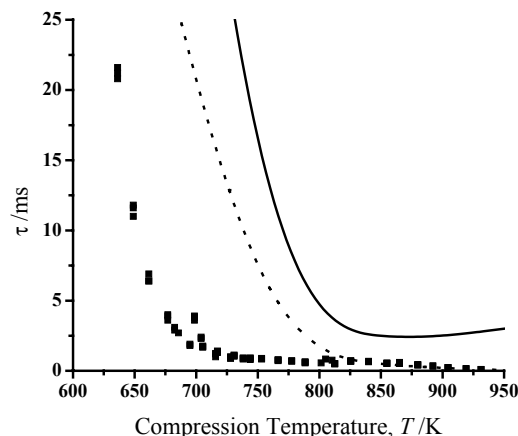


Fig. 6 n-Heptane, $\phi = 1.0$, $p_c = 15$ atm: Galway experimental (points), updated mechanism with reaction class 1 (solid line), updated mechanism with addition of reaction class 1 and 2 [O₂QOOH = Cyclic Ether + OH] (dotted line).

Reaction Class 3: RO₂ + OH → RO + HO₂

Reaction class 3 involves the reaction of an alkyl-peroxyl radical with a hydroxyl radical to produce an alkoxy radical and a hydroperoxyl radical. DeSain *et al.* [19] studied the reaction C₂H₅O₂ + OH = C₂H₅O + HO₂ by measuring OH concentration histories and recommended a rate constant expression of $2 \times 10^{13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. We have employed his rate constant expression for all reactions in this class. Addition of this reaction proved to be completely insensitive with no change in predicted ignition delay times in the range of experiments performed here.

Reaction Class 4: $\text{RO}_2 + \text{HO}_2 \rightarrow \text{ROOH} + \text{O}_2$

Reaction class 4 involves the reaction of an alkylperoxy radical with a hydroperoxy radical to produce two stable products — an alkylhydroperoxide species and molecular oxygen. Lightfoot *et al.* [20] studied the reaction $\text{CH}_3\text{O}_2 + \text{HO}_2 = \text{CH}_3\text{O}_2\text{H} + \text{O}_2$ and reported a rate constant of $2.47 \times 10^{11} \exp(-1,570 \text{ cal/RT}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which we have employed for all reactions in this class. However, this reaction class again proved to be insensitive in that no change in predicted ignition delay times were recorded in the temperature range 625–950 K.

Reaction Class 5: $\text{RO}_2 \rightleftharpoons \text{QOOH}$

Inclusion of reaction classes 1 and 2 led to shorter ignition delay times at low temperatures and improved the model agreement with experiments, but simulated ignition delay times were still consistently slower than experiment in the temperature range 625–775 K.

Recently, Raman *et al.* [21] have carried out *ab-initio* calculations at the CBS-QB3 level of theory for a series of many different five-, six-, seven- and eight-membered transition states involving alkylperoxy radicals. These rate constant expressions have been employed here for n-heptylperoxy radical isomerizations to hydroperoxy radicals. Fig. 7 depicts the model predicted and experimental ignition delay times in the temperature range 625–950 K.

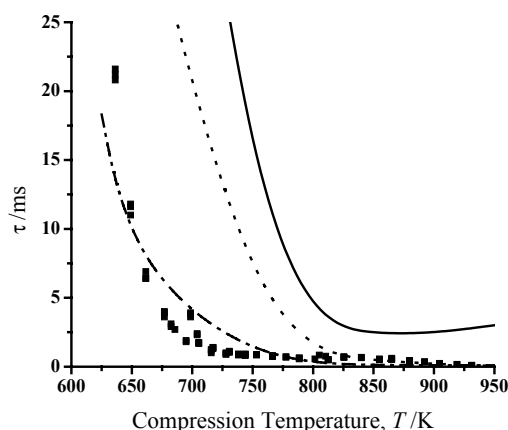


Fig. 7 n-Heptane, $\Phi = 1.0$, $p_c = 15$ atm: Galway experimental (points), updated mechanism with reaction class 1 (solid line), updated mechanism plus reaction class 1 and 2 (dotted line), updated mechanism plus reaction class 1, 2, and 5 (dash—dot line).

These rate constant expressions of Raman *et al.* lead to a substantial decrease in ignition delay times at low temperatures resulting in a substantial improvement in predictability of the detailed chemistry at low temperatures.

Reaction Class 6: $\text{O}_2\text{QOOH} \rightleftharpoons \text{Ketohydroperoxide} + \text{OH}$

The rate constant expressions of Raman *et al.* [21] were also employed for the second isomerization step, O_2QOOH forming a ketohydroperoxide species and a hydroxyl radical.

We combined these new rate expressions with the additional chemistry for reaction classes 1 and 2, described above and with the rate changes applied for reaction class 5 but found that the predicted ignition delay times were identical to those determined for the addition of reaction classes 1, 2 and 5 alone.

Previously, Curran *et al.* [16,17] had argued that the hydrogen atom undergoing this isomerization is weaker than a typical hydrogen atom in a hydrocarbon species and is more easily abstracted since it is bound to a carbon atom, which in turn is bound to a hydroperoxy group and therefore the activation energy was reduced by 3 kcal mol⁻¹. We have found that lowering the activation energies of Raman *et al.* by 1 kcal mol⁻¹ had no effect on predicted ignition delay times.

Within this study, the mechanism has only been validated at 10 and 15 atm and in the temperature range 625–950 K. We intend to extend this validation over a wider range of temperature and pressure in order to improve predictive capability using other available experimental data in the literature.

Conclusions

We have successfully shown that the addition of more detailed chemistry to the mechanism of Curran *et al.* from 2002 has improved the simulation of the NUIG RCM data at 15 atm [8].

The influence of the final reaction class of QOOH intra-isomerizations will be studied and their influence on mechanism predictions will then be reported.

Extensive validation of all these reaction class investigations has yet to be carried out using additional experimental data, other than our own RCM data. Once the mechanism for n-heptane is accurately reproducing low temperature chemistry such as that observed in these RCM studies, we will apply the same set of reaction class rules and knowledge gained to the remaining eight heptane isomers.

Acknowledgements

We acknowledge gratefully support from Enterprise Ireland under their Basic Research Grants Scheme and the receipt of the NUI, Galway—University of California Student Exchange Scholarship Program.

References

- [1] J. F. Griffiths, P. A. Halford-Maw, D. J. Rose, *Combust. Flame*, 95:291–306 (1993).
- [2] R. Minetti, M. Carlier, M. Ribaucour, E. Therssen, and L. R. Socher, *Combust. Flame*, 102:298–309 (1995).

- [3] R. Minetti, M. Carlier, M. Ribaucour, E. Therssen, and L. R. Sochet, *Proc. Combust. Inst.* 26:747—753 (1996).
- [4] A. Cox, J. F. Griffiths, C. Mohamed, H. J. Curran, W. J. Pitz, and C. K. Westbrook, *Proc. Combust. Inst.* 26:2685—2692 (1996).
- [5] J. F. Griffiths, P. A. Halford-Maw, C. Mohamed, *Combust. Flame*, 111:327—337 (1997).
- [6] C. Mohamed, *Combust. Flame*, 112:438—444 (1998).
- [7] C.S. McEnally, D.M. Ciuparu, L.D. Pfefferle, *Combust. Flame* 134:339—353 (2003).
- [8] E.J. Silke, H.J. Curran & J.M. Simmie, *Proc. Combust. Inst.* Paper 2E07, *in press* (2004).
- [9] C.K. Westbrook, W.J. Pitz, H.J. Curran, J. Boercker, E. Kunrath, *Int. J. Chem. Kin.* 33:868—877 (2001).
- [10] C.K. Westbrook, W.J. Pitz, H.J. Curran, J. Boercker, J.F. Griffiths, C. Mohamed & M. Ribaucour, *Proc. Combust. Inst.* 29 1311—1318 (2002).
- [11] J.M. Simmie, *Prog. Energy Combust. Sci.* 29 599—634 (2003).
- [12] J. Würmel, *PhD Thesis*, NUI, Galway (2004).
- [13] C.M. Lund and L. Chase “HCT - A General Computer Program for Calculating Time-Dependent Phenomena Involving One-Dimensional Hydrodynamics, Transport, and Detailed Chemical Kinetics”, Lawrence Livermore National Laboratory report UCRL—52504, revised (1995).
- [14] E.R. Ritter and J. W. Bozzelli, *Int. J. Chem. Kin.* 23:767—778 (1991).
- [15] S. W. Benson, *Thermochemical Kinetics*, John Wiley & Sons, New York (1976).
- [16] H.J. Curran, P. Gaffuri, W.J. Pitz and C.K. Westbrook, *Combust. Flame* 114:149—177 (1998).
- [17] H.J. Curran, P. Gaffuri, W.J. Pitz and C.K. Westbrook, *Combust. Flame* 129:253—280 (2002).
- [18] C. K. Westbrook, *Proc. Combust. Inst.* 28 1563-1577 (2000).
- [19] J.D. DeSain, S.J. Klippenstein, J.A. Miller and C.A. Taajes, *J. Phys. Chem. A* 107:4415—4427 (2003).
- [20] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat and F. Zabel, *Atmos. Environ. Part A*: 26:1805—1961 (1992).
- [21] S. Raman, W.H. Green and W.J. Pitz, private communication (2004).